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(54) Title: POLYESTER FILM (57) Abstract A polyester film has the following shrinkage properties (i) a degree of shrinkage at 70 °C of less than 15 %, (ii) a degree of shrinkage at 100 °C of greater than 30 %, (iii) a ratio of shrinkage at 100 °C in one direction to the other perpendicular direction in the range from 4:1 to 1:1. The polyester film is particularly suitable for wrapping hot food products.		

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Polyester Film

This invention relates to a polyester film and, in particular, to a heat-shrinkable polyester film.

Shrinkable polymeric films have been made from polyvinyl chloride, polystyrene, polyolefine, such as polyethylene and polypropylene, and polyester. Shrinkable polymeric films have been used for a wide range of packaging and labelling applications. In particular, shrinkable polymeric films have been used as labels for polyethylene terephthalate (PET) drinks bottles, and for tamper proof labelling on food and pharmaceutical products.

There has been little use of shrinkable polymeric films for direct packaging of food products, ie where the film is in actual contact with the food. One such example is the use of shrinkable polyolefine films for wrapping raw meat products prior to freezing. There has been little or no commercial use of shrinkable polymeric films for packaging hot, ie cooked food products. There would be a significant convenience advantage to the purchaser of such products, if they could be re-heated, prior to consumption, in the same film in which they were originally packaged. A wide range of food, particularly meat products such as legs of lamb, pork etc, poultry such as whole chickens etc, could be cooked, and sealed by wrapping in shrinkable film while hot, in order to preserve juices, texture and flavour. These cooked and packaged food products could then be rapidly cooled, transported to the shop or supermarket, and sold to the consumer, who would be able to re-heat the food in a microwave or conventional oven in the original packaging film.

GB-A-825549 is directed to a shrinkable copolyester film produced by either monoaxial or biaxial stretching. The copolyester film is formed from ethylene terephthalate and ethylene isophthalate. The films exhibit significant degrees of shrinkage at temperatures as low as 70 or 80°C.

EP-A-0210648 discloses a shrinkable polyester film which can be formed into a tube for shrinking on to bottles. The films possess unbalanced shrinkage properties, having a high degree of shrinkage in one direction and a low degree of shrinkage in the other perpendicular direction.

WO-95/14734 is directed to a shrinkable film formed from a polyester/plasticiser blend which shrinks at very low temperatures and has a low rate of shrinkage.

Unfortunately existing shrinkable films do not possess the required properties for packaging hot, particularly food, products. In particular prior art films may exhibit, inter alia, (i) insufficient shrinkage, (ii) unbalanced shrinkage, ie shrinkage in one

direction is significantly greater than shrinkage in the other perpendicular direction, (iii) shrinkage occurring at too low a temperature, (iv) lack of stability at high temperatures, eg on re-heating, (v) insufficient physical properties, such as brittleness, and (vi) poor heat-sealing properties. The use of prior art films having one or more of the
5 aforementioned properties may lead to uneven shrinking over hot food products resulting in unattractive film wrinkling and distortion, inefficient sealing of the film and consequent leakage of material during subsequent handling and re-heating.

It is well known to prepare a polyester in a two stage process. In the first stage monomer is produced at a temperature in the range from 150 to 285°C generally by
10 reacting a dicarboxylic acid with a glycol (direct esterification) or alternatively by reacting an alkyl ester of a dicarboxylic acid with a glycol (ester interchange). A catalyst such as manganese acetate or zinc acetate is normally employed in the ester interchange reaction, whereas direct esterification can be carried out in the absence of a catalyst. In the second stage of polyester production the monomer molecules are
15 condensed together (polycondensation) by heat in the presence of a catalyst. Glycol is produced during the condensation reaction and removed under reduced pressure. A wide range of polycondensation catalysts have been employed commercially such as antimony trioxide, germanium dioxide and zinc acetate. Antimony has been the preferred polycondensation catalyst. Unfortunately there are increasing environmental
20 concerns about the use of antimony, and the use thereof is likely to be restricted in the future, including limits on the disposal of antimony-containing wastes. There is thus a need to be able to commercially prepare polyester by means of an antimony-free catalyst composition, particularly for when used to prepare film for food contact applications.

25 We have now devised a shrinkable polyester film which reduces or substantially overcomes at least one of the aforementioned problems.

Accordingly, the present invention provides a polyester film having the following shrinkage properties (i) a degree of shrinkage at 70°C of less than 15%, (ii) a degree of shrinkage at 100°C of greater than 30%, (iii) a ratio of shrinkage at 100°C in
30 one direction to the other perpendicular direction in the range from 4:1 to 1:1.

The invention also provides a method of producing a polyester film which comprises forming a polyester film having the following shrinkage properties (i) a degree of shrinkage at 70°C of less than 15%, (ii) a degree of shrinkage at 100°C of greater than 30%, (iii) a ratio of shrinkage at 100°C in one direction to the other
35 perpendicular direction in the range from 4:1 to 1:1.

The polyester film according to the present invention is suitably formed from any synthetic thermoplastic polyester, particularly a synthetic linear polyester which may be obtained by condensing one or more dicarboxylic acids or their lower alkyl (up to 6 carbon atoms) diesters, eg terephthalic acid, isophthalic acid, phthalic acid, 2,5-,
5 2,6- or 2,7-naphthalenedicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, 1,2-, 1,3- or 1,4-cyclohexane dicarboxylic acid, 4,4'-diphenyldicarboxylic acid, hexahydro-terephthalic acid or 1,2-bis-p-carboxyphenoxyethane (optionally with a monocarboxylic acid, such as pivalic acid) with one or more glycols, particularly aliphatic glycols, eg ethylene glycol, diethylene glycol, triethylene glycol,
10 1,3-propanediol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 2,2-dimethyl 1,3-propane diol, neopentyl glycol and 1,4-cyclohexanedimethanol.

The dicarboxylic acid component of the polyester preferably comprises in the range from 50 to 100, more preferably 60 to 98, particularly 70 to 95, and especially 75 to 90 mole % of terephthalic acid or esters thereof. At least one or more additional
15 aromatic or aliphatic dicarboxylic acids may also be used, preferably isophthalic acid or esters thereof. A particularly preferred dicarboxylic acid combination is from 75 to 85 mole % terephthalic acid and from 15 to 25 mole % isophthalic acid.

The glycol component of the polyester preferably comprises at least 70, more preferably at least 80, and particularly at least 90 and up to 100 mole % of ethylene
20 glycol. Other preferred glycol components include diethylene glycol and 1,4-cyclohexanedimethanol. A particularly preferred glycol combination is from 95 to 100 mole % ethylene glycol and from 0 to 5 mole % diethylene glycol.

Preferred polyesters are copolyesters of ethylene terephthalate and ethylene isophthalate, preferably comprising from 60 to 95 mole % ethylene terephthalate and
25 from 5 to 40 mole % ethylene isophthalate. Particularly preferred copolyesters comprise from 65 to 90 mole %, more preferably 75 to 85 mole % ethylene terephthalate and from 10 to 35 mole %, more preferably 15 to 25 mole % ethylene isophthalate, and especially a copolyester of about 80 mole % ethylene terephthalate and about 20 mole % ethylene isophthalate.

30 The polyester is preferably produced using a catalyst composition comprising 10 to 150 ppm of titanium atoms and 10 to 100 ppm of phosphorus atoms, both based on the weight of the final polyester.

Suitable titanium catalyst compounds include inorganic titanates such as sodium titanate and lithium titanate, and preferably organic titanates, more preferably
35 alkyl titanates, and particularly tetraalkyl titanates, wherein the alkyl group has 1 to 6 carbon atoms. Preferred titanates include tetramethyl titanate, tetraethyl titanate,

tetrapropyl titanate, tetraisopropyl titanate, tetrabutyl titanate and tetrahexyl titanate. Tetraisopropyl titanate is a particularly preferred titanate. Other suitable titanates include triethanolamine titanate, and the titanates of ethylene glycol, hexylene glycol and octylene glycol. Two or more of the aforementioned titanates may be used together.

The concentration of titanium atoms present in the catalyst composition is preferably in the range from 15 to 120, more preferably 20 to 100, particularly 30 to 90, and especially 40 to 80 ppm based on the weight of the final polyester.

The titanium compound may be added after monomer formation, but is preferably added prior to monomer formation, ie prior to the direct esterification or ester interchange reaction. Thus, the titanium compound is preferably catalysing at least the polycondensation reaction.

Suitable phosphorus compounds which primarily act as a stabiliser include phosphorus acids, phosphinic acids, phosphates and phosphites. Particular examples include phosphorous acid, phosphoric acid, phosphonic acid, sodium dihydrogen phosphate, tris nonylphenyl phosphite, trimethyl phosphate, triethyl phosphate, tributyl phosphate, triphenyl phosphate, diphenyl phosphite, dibutyl phosphite, dimethylphenyl phosphonate and ammonium phosphate. The phosphorus compound is preferably selected from the group consisting of phosphoric acid, phosphorous acid, and tris nonylphenyl phosphite.

The concentration of phosphorus atoms present in the catalyst composition is preferably in the range from 20 to 80, more preferably 30 to 70, particularly 40 to 60, and especially 45 to 55 ppm based on the weight of the final polyester.

The phosphorus compound may be added prior to monomer formation, but is preferably added after monomer formation, ie after the direct esterification or ester interchange reaction, and prior to the polycondensation reaction.

The ratio of titanium atoms to phosphorus atoms present in the catalyst composition is preferably in the range from 0.5 to 2.0, more preferably 0.75 to 1.5, particularly 0.9 to 1.2, and especially 1.0 to 1.1.

In a preferred embodiment of the invention the catalyst composition additionally comprises a blue toning material preferably in the range from 6 to 200, more preferably 15 to 140, particularly 30 to 80, and especially 40 to 60 ppm based on the weight of the final polyester. Cobalt is a preferred blue toning material, preferably added in salt form such as cobalt acetate.

The blue toning material is preferably added after monomer formation, ie after the direct esterification or ester interchange reaction, and prior to the

polycondensation reaction. The blue toning material is however, preferably added after the phosphorous compound.

5 The catalyst composition preferably comprises a diethylene glycol suppressant, such as sodium hydroxide, preferably in the range from 10 to 200, more preferably 30 to 70 ppm based on the weight of the final polyester. The diethylene glycol suppressant is preferably added prior to monomer formation, more preferably at the same time as the titanium compound.

10 The polyester preferably has an intrinsic viscosity (IV) in the range from 0.5 to 0.8, more preferably 0.6 to 0.7, and particularly 0.63 to 0.67. The polyester suitably exhibits a low IV drop on film extrusion, preferably less than 0.04, more preferably in the range from 0.001 to 0.03, particularly 0.005 to 0.02, and especially 0.01 to 0.015.

15 In a particularly preferred embodiment of the invention, the polyester has a colour "b" value (ie yellowness value) in the range from -5 to 15, more preferably -3 to 10, particularly 0 to 8, and especially 4 to 6.

20 The glass transition temperature (T_g) of the polyester is preferably in the range from 40 to 120°C, more preferably 50 to 100°C, particularly 60 to 90°C, and especially 70 to 80°C.

25 The melting point of the polyester is preferably in the range from 180 to 258°C, more preferably 200 to 240°C, particularly 205 to 230°C, and especially 210 to 220°C.

30 The polyester film is preferably biaxially oriented by sequential stretching in two mutually perpendicular directions, typically at a temperature in the range from 70 to 125°C. Formation of the film may be effected by any process known in the art for producing a polyester film, for example a tubular or a flat film process.

35 In a tubular process simultaneous biaxial orientation may be effected by extruding a thermoplastics polyester tube which is subsequently quenched, reheated and then expanded by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation.

40 In the preferred flat film process a film-forming polyester is extruded through a slot die and rapidly quenched upon a chilled casting drum to ensure that the polyester is quenched to the amorphous state. Orientation is then effected by stretching the quenched extrudate at a temperature above the glass transition temperature of the polyester. Sequential orientation may be effected by stretching a flat, quenched extrudate firstly in one direction, usually the longitudinal direction, ie the forward direction through the film stretching machine, known as the machine direction (MD), and then in the transverse direction (TD). Forward stretching of the extrudate is

conveniently effected over a set of rotating rolls or between two pairs of nip rolls, transverse stretching then being effected in a stenter apparatus. The polyester film is preferably stretched so that the dimension of the oriented film is from 2.0 to 4.0, more preferably 2.5 to 3.5, and particularly 2.7 to 3.1 times in the MD, and from 2.5 to 4.5, more preferably 3.0 to 4.0, and particularly 3.6 to 4.0 times in the TD.

The stretched film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional restraint preferably at a temperature above the glass transition temperature of the film-forming polyester but below the melting temperature thereof, to induce crystallisation of the polyester. The polyester film is suitably heat-set at a relatively low temperature, preferably from 60 to 150°C, more preferably 70 to 120°C, particularly 75 to 100°C, and especially 80 to 90°C.

In a preferred embodiment of the invention, the polyester film has a degree of shrinkage at 70°C of less than 10%, more preferably less than 5%, and particularly less than 2%. The polyester film suitably has a degree of shrinkage at 80°C of less than 20%, preferably less than 15%, more preferably less than 10%, particularly less than 5%, and especially less than 2%.

In addition, the polyester film suitably has a degree of shrinkage at 100°C of greater than 35%, preferably greater than 40%, more preferably greater than 45%, particularly greater than 50%, and especially greater than 55%. The polyester film suitably has a degree of shrinkage at 120°C of greater than 40%, preferably greater than 45%, more preferably greater than 50%, particularly greater than 55%, and especially greater than 60%.

The aforementioned shrinkage values are measured in air using the technique described herein. The degree of shrinkage refers to the mean value of shrinkage in the MD and TD film directions. In a preferred embodiment of the invention the shrinkage values in both the MD and TD directions is less than the above mentioned preferred values at 70°C, and more preferably also at 80°C. In a particularly preferred embodiment of the invention the shrinkage values in both the MD and TD directions is greater than the above mentioned preferred values at 100°C, and more preferably also at 120°C.

The ratio of shrinkage at 100°C in one direction to the other perpendicular direction is suitably in the range from 3:1 to 1:1, preferably 2.5:1 to 1:1, more preferably 2:1 to 1:1, particularly 1.5:1 to 1:1, and especially 1.2:1 to 1:1. By ratio of shrinkage is meant the degree of shrinkage in one direction (MD or TD, whichever is the highest value) divided by the degree of shrinkage in the other perpendicular direction (the other of MD or TD, whichever is the lowest value). Thus, polyester films

according to the present invention preferably possess balanced shrinkage properties, whereby the degree of shrinkage in the MD is approximately the same as the degree of shrinkage in the TD. Where the degree of shrinkage is greater in one direction than the other, it is preferred that the TD shrinkage is greater than the MD shrinkage.

5 The polyester film is preferably suitable for heat-sealing to itself by using conventional heat-sealing apparatus and conditions, whereby the seal is formed by heating two or more layers of the polyester film to a temperature at which the polyester is softened or melted, resulting in a heat-seal bond being formed. The polyester film preferably exhibits a heat-seal strength, measured by sealing the film to itself, in the
10 range from 200 to 1500, more preferably 300 to 1200, and particularly 400 to 1000 Nm^{-1} .

 The polyester film preferably has a degree of crystallinity in the range from 2% to 20%, more preferably 4% to 15%, and particularly 6% to 10%.

 In one embodiment of the invention the polyester film is transparent, exhibiting
15 high optical clarity and low haze, preferably having a wide angle haze, being measured according to the standard ASTM D 1003-61, of <8%, more preferably <6%, particularly <5%, and especially <3%, preferably for a 40 μm thick film. The aforementioned optical characteristics can be suitably achieved by having little or no particulate additive present in the film. The polyester film may contain relatively small quantities
20 of filler material in order to provide handleability, for example in the range from 5 to 3000 ppm, preferably 50 to 2000 ppm, and more preferably 100 to 1000 ppm. Suitable fillers include inorganic materials such as silica, china clay, calcium carbonate, and organic materials such as silicone resin particles. Spherical monodisperse fillers are preferred.

25 However, in an alternative embodiment of the invention the polyester film is opaque, which is defined as a film exhibiting a Transmission Optical Density (Sakura Densitometer; type PDA 65; transmission mode) of from 0.75 to 1.75, and particularly of from 1.2 to 1.5, preferably for a 40 μm thick film. The polyester film is conveniently rendered opaque by incorporating into the polyester, an effective amount of an
30 opacifying agent. Suitable opacifying agents include an incompatible resin filler, a particulate inorganic filler or a mixture of two or more such fillers.

 By an "incompatible resin" is meant a resin which either does not melt, or which is substantially immiscible with the polyester, at the highest temperature encountered during extrusion and fabrication of the film. The presence of an
35 incompatible resin usually results in a voided film, by which is meant comprises a cellular structure containing at least a proportion of discrete, closed cells. Suitable

incompatible resins include polyamides and olefin polymers, particularly a homo- or co-polymer of a mono- α -olefin containing up to 6 carbon atoms in its molecule, for incorporation into polyester. Preferred materials include a low or high density olefin homopolymer, particularly polyethylene, polypropylene or poly-4-methylpentene-1, an olefin copolymer, particularly an ethylene-propylene copolymer, or a mixture of two or more thereof. Random, block or graft copolymers may be employed.

The amount of incompatible resin filler present in the polyester film is preferably in the range from 2% to 30%, more preferably 3% to 20%, particularly 4% to 15%, and especially 5% to 10% by weight, based on the weight of the polyester.

Particulate inorganic fillers suitable for generating an opaque polyester film include conventional inorganic pigments and fillers, and particularly metal or metalloid oxides, such as alumina, silica and titania, and alkaline metal salts, such as the carbonates and sulphates of calcium and barium. The particulate inorganic fillers may be of the voiding or non-voiding type. Suitable particulate inorganic fillers may be homogeneous and consist essentially of a single filler material or compound, such as titanium dioxide or barium sulphate alone. Alternatively, at least a proportion of the filler may be heterogeneous, the primary filler material being associated with an additional modifying component. For example, the primary filler particle may be treated with a surface modifier, such as a pigment, soap, surfactant coupling agent or other modifier to promote or alter the degree to which the filler is compatible with the polyester.

The volume distributed median particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the particles, read on the cumulative distribution curve relating volume % to the diameter of the particles - often referred to as the "D(v,0.5)" value) of the inorganic filler, preferably titanium dioxide, is preferably in the range from 0.2 to 5 μm , more preferably 0.4 to 1.5 μm , and particularly 0.8 to 1.2 μm .

The size distribution of the inorganic filler particles is also an important parameter, for example the presence of excessively large particles can result in the film exhibiting unsightly 'speckle', ie where the presence of individual filler particles in the film can be discerned with the naked eye. It is preferred that none of the inorganic filler particles incorporated into the polyester film should have an actual particle size exceeding 30 μm . Particles exceeding such a size may be removed by sieving processes which are known in the art. However, sieving operations are not always totally successful in eliminating all particles greater than a chosen size. In practice, therefore, the size of 99.9% by number of the inorganic filler particles should not

exceed 30 μm , preferably should not exceed 20 μm , and more preferably should not exceed 15 μm . Preferably at least 90%, more preferably at least 95% by volume of the inorganic filler particles are within the range of the volume distributed median particle diameter $\pm 0.8 \mu\text{m}$, and particularly $\pm 0.5 \mu\text{m}$.

5 The amount of inorganic filler, particularly of titanium dioxide, incorporated into the polyester film should be not less than 1% nor exceed 30% by weight, based on the weight of the polyester. Particularly satisfactory levels of opacity are achieved when the concentration of filler is in the range from about 5% to 20%, preferably 10% to 15%, and more preferably 12% to 13% by weight, based on the weight of the
10 polyester. The preferred titanium dioxide particles may be of anatase or rutile crystal form.

Particle size of the filler particles may be measured by electron microscope, coulter counter, sedimentation analysis and static or dynamic light scattering. Techniques based on laser light diffraction are preferred. The median particle size may
15 be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile.

The thickness of a polyester film according to the invention is preferably in the range from 5 to 150 μm , more preferably 15 to 100 μm , particularly 20 to 70 μm , and especially 30 to 50 μm .

20 A polyester film according to the invention may be coated on one or both surfaces with one or more additional coating, ink, lacquer and/or metal layers, for example to form a laminate or composite which exhibits improved properties, such as handleability, antistatic, adhesion promoting or release, compared with the component materials. Suitable coating materials include film-forming polymeric resins such as
25 acrylic resins, copolyesters, styrene copolymers, acrylic copolymers, functionalised polyolefins, polyvinyl alcohol, cellulosic materials such as nitrocellulose, ethylcellulose and hydroxyethylcellulose. Blends or mixtures of any of the aforementioned polymeric resins may be employed.

Prior to the deposition of a coating medium onto the polyester film, the
30 exposed surface thereof may, if desired, be subjected to a chemical or physical surface-modifying treatment to improve the bond between that surface and the subsequently applied coating layer. A preferred treatment is corona discharge. Alternatively, the surface of the polyester film may be pre-treated with an agent known in the art to have a solvent or swelling action thereon, such as a halogenated phenol
35 dissolved in a common organic solvent eg a solution of p-chloro-m-cresol,

2,4-dichlorophenol, 2,4,5- or 2,4,6-trichlorophenol or 4-chlororesorcinol in acetone or methanol.

5 The coating medium may be applied to an already oriented polyester film surface, but application of the coating medium is preferably effected before or during the stretching operation. In particular, it is preferred that the coating medium should be applied to the polyester film surface between the two stages (longitudinal and transverse) of a biaxial stretching operation.

10 The polyester film, or additional coating layer, may conveniently contain any of the additives conventionally employed in the manufacture of polymeric films. Thus, agents such as dyes, pigments, voiding agents, lubricants, anti-oxidants, anti-blocking agents, surface active agents, slip aids, gloss-improvers, prodegradants, ultra-violet light stabilisers, viscosity modifiers and dispersion stabilisers may be incorporated into the film-forming polyester and/or coating layer medium.

15 The invention is illustrated by reference to the following examples
The following test procedures were used.

1) Thermal shrinkage was determined by heating 10 cm strips of film in an oven at temperatures of 70, 80, 90, 100 and 120°C for 1 minute. The mean percentage reduction in length of 5 samples was calculated. Separate strips of film were used to determine the shrinkage in the MD and TD. The 1 minute time period was chosen to ensure that maximum shrinkage, ie at that particular temperature, had occurred.

2) Intrinsic viscosity (IV) of the polyester was measured by solution viscosity of an 8% solution of polyester in orthochlorophenol at 25°C.

3) The melting point, glass transition temperature (T_g) and crystallinity of the polyester were determined by Differential Scanning Calorimetry.

25 4) A heat-seal was formed by positioning together and heating two layers of film at 220°C for one second under a pressure of 103 kPa (15 psi). The sealed film was cooled to room temperature, and the heat-seal strength determined by measuring the force required under linear tension per unit width of seal to peel the layers of the film apart at a constant speed of 4.23 mm/second.

30 Example 1

The film polyester was made by using a batch terephthalic acid based route. The esterification vessel was charged with 1810 Kg of terephthalic acid (80.5 mole %), 440 Kg of isophthalic acid (19.5 mole %), 1050 litres of ethylene glycol, 50 ppm of sodium hydroxide and 500 ppm of tetraisopropyl titanate (TIPT). The mixture was heated at 230 to 240°C until all the water had been distilled off. 165 ppm of phosphoric acid stabiliser was then added, and the reaction mixture transferred to an autoclave.

300 ppm of cobalt acetate tetrahydrate was added, the reaction mixture was heated to 295°C and polymerisation under vacuum occurred. The final polyester product had an intrinsic viscosity (IV) of 0.67.

5 A molten web of the polyester prepared above was extruded in a conventional manner from a slot die on to the polished surface of a cooled rotating drum upon which the web was quenched to below the glass transition temperature of the polyester to provide an amorphous film. The quenched film was then reheated and drawn about 2.9 times its original length in the MD at a temperature of about 80°C. The polyester film was passed into a stenter oven which had a temperature in the pre-heat zone of 10 about 85°C, and the sheet stretched in the TD to approximately 3.8 times its original dimensions. The temperature in the stretching zone of the stenter oven was about 105°C. The biaxially stretched polyester film was heat set at a temperature of about 80°C. Final film thickness was 40 µm.

15 The polyester film was subjected to the test procedures described herein and exhibited the following properties:

(i) Thermal Shrinkage

			Temperature (°C)					
			70	80	90	100	110	120
20	<u>%</u>	MD	0	2.2	27	38	41	45
	<u>Shrinkage</u>	TD	0	1.9	47	57	60	60

(ii) Intrinsic Viscosity = 0.66, ie the IV drop on film extrusion was 0.01.

(iii) Melting Point = 215°C, Tg = 75°C and Crystallinity = 8%.

(iv) Heat-Seal Strength = 400 Nm⁻¹.

25 A whole chicken was cooked in an oven in traditional manner, and placed directly from the oven on to the polyester film produced above. A second polyester film was placed over the top of the chicken and the two films heat-sealed together at 220°C under vacuum in order to form a bag in which the chicken was completely enveloped. The packaged chicken was then placed in an oven at a temperature of 100 to 120°C in order for shrinkage of the polyester film surrounding the chicken to occur. 30 After removal from the oven and subsequent cooling, the appearance of the shrunken polyester film surrounding the chicken was examined. The polyester film possessed no creases or wrinkles, ie had evenly shrunk over the chicken and was of excellent appearance.

35 The shrink wrapped chicken was then re-heated in a conventional oven for 45 minutes. The polyester film surrounding the re-heated chicken maintained its integrity,

ie the seal remained intact and there was no leakage of contents, and excellent appearance, ie no creases or wrinkles formed during the re-heating process.

Example 2

This is a comparative Example not according to the invention.

5 The procedure of Example 1 was repeated except that the MD stretching ratio was 1.0 (ie no stretching), the TD stretching ratio was 4.0, and the heat-setting temperature was about 55°C.

The polyester film was subjected to the test procedures described herein and exhibited the following properties:

10 (i) Thermal Shrinkage

		<u>Temperature (°C)</u>					
		70	80	90	100	110	120
<u>%</u>	MD	0	3	3	5	8	8
<u>Shrinkage</u>	TD	5	42	57	62	65	65

15 (ii) Intrinsic Viscosity = 0.66, ie the IV drop on film extrusion was 0.01.

(iii) Melting Point = 215°C, Tg = 75°C and Crystallinity = 6%.

(iv) Heat-Seal Strength = 400 Nm⁻¹.

The appearance of the shrunken polyester film surrounding the chicken was poor exhibiting a significant number of wrinkles and creases.

20 Example 3

This is a comparative Example not according to the invention.

The procedure of Example 1 was repeated except that polyethylene terephthalate homopolymer was used.

25 The polyester film was subjected to the test procedures described herein and exhibited the following properties:

(i) Thermal Shrinkage

		<u>Temperature (°C)</u>					
		70	80	90	100	110	120
<u>%</u>	MD	0	0.8	9	20	27	28
<u>Shrinkage</u>	TD	0	1.3	12	30	43	48

30

(ii) Intrinsic Viscosity = 0.61, ie the IV drop on film extrusion was 0.04.

(iii) Melting Point = 260°C, Tg = 79°C and Crystallinity = 22%.

(iv) Heat-Seal Strength = 0 Nm⁻¹.

The degree of shrinkage of the polyester film was insufficient to adequately shrink over the chicken. In addition, a heat-seal was not formed.

Example 4

This is a comparative Example not according to the invention.

5 The procedure of Example 1 was repeated except that polyethylene terephthalate homopolymer was used, the stenter pre-heat zone temperature was about 85°C, and the stenter stretching zone temperature was about 105°C.

The polyester film was subjected to the test procedures described herein and exhibited the following properties:

10 (i) Thermal Shrinkage

		<u>Temperature (°C)</u>					
		70	80	90	100	110	120
<u>%</u>	MD	0	0.5	5.5	12	16	17
<u>Shrinkage</u>	TD	0	0.8	7.3	18	26	29

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(ii) Intrinsic Viscosity = 0.61, ie the IV drop on film extrusion was 0.04.

(iii) Melting Point = 260°C, Tg = 79°C and Crystallinity = 22%.

(iv) Heat-Seal Strength = 0 Nm⁻¹.

20 The degree of shrinkage of the polyester film was insufficient to adequately shrink over the chicken. In addition, a heat-seal was not formed.

Example 5

This is a comparative Example not according to the invention.

25 The procedure of Example 1 was repeated except that the stenter pre-heat zone temperature was about 85°C, the stenter stretching zone temperature was about 105°C and the heat-setting temperature was about 90°C.

The polyester film was subjected to the test procedures described herein and exhibited the following properties:

(i) Thermal Shrinkage

		<u>Temperature (°C)</u>					
		70	80	90	100	110	120
<u>%</u>	MD	0	0.3	4.4	14.5	23	24
<u>Shrinkage</u>	TD	0	5.8	30	42	53	55

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(ii) Intrinsic Viscosity = 0.66, ie the IV drop on film extrusion was 0.01.

(iii) Melting Point = 215°C, Tg = 75°C and Crystallinity = 8%.

35 (iv) Heat-Seal Strength = 400 Nm⁻¹.

The degree of shrinkage of the polyester film was insufficient to adequately shrink over the chicken.

The above results illustrate that a polyester film according to the present invention provides improved heat-shrinkable properties.

Claims

1. A polyester film having the following shrinkage properties (i) a degree of shrinkage at 70°C of less than 15%, (ii) a degree of shrinkage at 100°C of greater than 30%, (iii) a ratio of shrinkage at 100°C in one direction to the other perpendicular direction in the range from 4:1 to 1:1.
2. A polyester film according to claim 1 wherein the melting point of the polyester is in the range from 180 to 258°C.
3. A polyester film according to either one of claims 1 and 2 wherein the degree of shrinkage at 80°C is less than 20%.
4. A polyester film according to any one of the preceding claims wherein the degree of shrinkage at 120°C is greater than 40%.
5. A polyester film according to any one of the preceding claims wherein the ratio of shrinkage at 100°C in one direction to the other perpendicular direction in the range from 2:1 to 1:1.
6. A polyester film according to any one of the preceding claims wherein the polyester has a colour "b" value in the range from -5 to 15.
7. A polyester film according to any one of the preceding claims wherein the film comprises 10 to 150 ppm of titanium atoms and 10 to 100 ppm of phosphorus atoms, both based on the weight of the polyester.
8. A polyester film according to any one of the preceding claims wherein the film has a degree of crystallinity in the range from 4% to 15%.
9. A polyester film according to any one of the preceding claims wherein the film has a heat-seal strength, measured by sealing the film to itself, in the range from 200 to 1500 Nm⁻¹.
10. A method of producing a polyester film which comprises forming a polyester film having the following shrinkage properties (i) a degree of shrinkage at 70°C of less than 15%, (ii) a degree of shrinkage at 100°C of greater than 30%, (iii) a ratio of shrinkage at 100°C in one direction to the other perpendicular direction in the range from 4:1 to 1:1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/08638

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/183

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 825 549 A (DU PONT DE NEMOURS) 16 December 1959 (1959-12-16) cited in the application	1-5,8,10
Y	claims 1-7; example 24 ---	6
Y	US 4 447 595 A (SMITH RICHARD R ET AL) 8 May 1984 (1984-05-08) column 6, line 55-65 -----	6



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

21 July 1999

Date of mailing of the international search report

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-6,8,10

2. Claim : 7

3. Claim : 9

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/ 08638

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 6, 8, 10

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/08638

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 825549	A	NONE	
US 4447595	A	08-05-1984	
		BR 8304625 A	24-04-1984
		CA 1231195 A	05-01-1988
		DE 3376329 A	26-05-1988
		EP 0102913 A	14-03-1984
		JP 59059721 A	05-04-1984
		ZA 8306270 A	25-04-1984